

Application of Dynamic Light Scattering to Characterize Nanoparticle Agglomeration in Alumina Nanofluids and its Effect on Thermal Conductivity

Bridget L. Dwornick¹, Nigil S. Jeyashekar^{2*}, James E. Johnson^{2,3}, J. David Schall⁴, Allen S. Comfort¹, Qian Zou⁴, James S. Dusenbury¹, Steven J. Thrush^{4,1}, Christopher C. Powers^{4,1}, Scott A. Hutzler², Edwin A. Frame²

¹US Army RDECOM TARDEC, 6501 East 11 Mile Road, Warren, Michigan, 48397; ^{2*}Southwest Research Institute, US Army TARDEC Fuels and Lubricants Research Facility (TFLRF), 6220 Culebra Road, Bldg 140, San Antonio, Texas, 78238; ³University of Texas at San Antonio, One UTSA Circle, San Antonio, Texas, 78249; ⁴Oakland University, Rochester, Michigan, 48309

^{2*}Phone: 210-522-2533

^{2*}Fax: 210-522-3270

^{2*}Email: nigil.jeyashekar@swri.org

¹<http://www.tardec.army.mil>, ^{2*}<http://www.swri.org/4org/d08/d08home.htm>, ³<http://www.utsa.edu>
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Abstract

Nanoparticles dispersed in base fluids have shown that they have increased thermal conductivity and increased heat transfer potential. In practical applications, these particles agglomerate in nanofluid to form aggregates, as opposed to completely dispersing in the base fluid. The resulting nanofluid has a size distribution of aggregated nanoparticles at different length scales. The mechanism that causes the enhanced thermal characteristics in nanofluids has not been widely researched in terms of particle interactions and experimental characterization of aggregate size distribution. This study reports nanofluid characterization by Dynamic Light Scattering (DLS) measurements at dilute and regular particle concentrations. In this study, the resulting size distribution data was used to determine thermal conductivity enhancement by mechanisms of aggregation and liquid layering around nanoparticles using fractal models. These thermal conductivity results were compared with results based on the Maxwell model, which signified a completely dispersed nanofluid. It was determined by this study that nanoparticle aggregation results in the formation of percolation clusters and liquid layers that cause the thermal conductivity of dilute and regular nanofluids to increase 2.5 fold compared to results using a well-dispersed nanofluid. It was also determined that liquid layering did not significantly contribute to enhancement in thermal conductivity of the nanofluid, in addition to percolation clusters. The study concluded that the near-linear relationship between particle concentration and thermal

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Keywords

nanofluids, Dynamic Light Scattering, fractal dimension, nanocluster, nanolayer, thermal conductivity

Introduction

Coolants and cooling systems have been identified as important areas of research in ground vehicle science. Fluids containing nanometer-sized particles, known as nanofluids, have been shown to have increased thermal conductivity and heat transfer potential (Choi, 1995). Nanofluids have the potential to enhance thermal efficiencies in ground vehicles by improving heat rejection to ambient air and yield better performing vehicles. A model for thermal conductivity of fluids in which small spheres are uniformly dispersed was formulated by James Maxwell (Maxwell, 1873). In the Maxwell model, the thermal conductivity of the nanofluid, k_{eff} (Equation 1) is based on the total particle volume fraction, ϕ , and thermal conductivities of particle, k_p , and base fluid, k_f .

$$\frac{k_{eff}}{k_f} = \frac{(1 - \phi) + 3\phi \frac{k_p}{k_p + 2k_f}}{(1 - \phi) + 3\phi \frac{k_f}{k_p + 2k_f}} \rightarrow (1)$$

In the above model, the thermal conductivity of the nanofluid increases linearly with particle volume fraction. For alumina nanoparticles that are completely dispersed in de-ionized water, the Maxwell model predicts that the thermal conductivity enhancement varies between 0.28 and 31.18 percent for particle volume fractions between 0.1 and 10 percent, at 20°C. However, comprehensive literature review of experimental and theoretical studies on alumina nanofluids have shown thermal conductivity enhancements higher than that predicted by the Maxwell model (Özerinç *et al.*, 2009). It was proposed that the increase in thermal conductivity is caused by the agglomeration of nanoparticles in the base fluid (Venerus and Jiang, 2011). Hence, there is a need to understand the agglomeration characteristics of nanoparticles in base fluids, and determine their impact on thermal conductivity. Also, there is limited experimental data on thermal conductivity of nanofluids below 1 percent by volume of nanoparticles and, at such low concentrations, nanofluids have shown anomalous increase in thermal

conductivity (Choi, 2009). Thus, this paper will emphasize alumina nanofluids with volume fractions at 0.2 percent and 1 percent in an effort to understand the relationship between agglomeration of nanoparticles in base fluid and thermal conductivity at dilute and regular nanoparticle volume fractions.

Theoretical Models for Thermal Conductivity

Nanoparticles that are dispersed in base fluid are in a constant state of random Brownian motion. For stationary nanofluid, this random motion of nanoparticles results in the formation of aggregates or clusters. The formation of aggregates depends on the short-range interparticle potential and sticking probability of either two particles, or particles and aggregates, or two aggregates (Prasher *et al.*, 2006). The dynamics of irreversible aggregate formation could be either diffusion-limited or reaction-limited. Both aggregation mechanisms result in the formation of clusters of different radii (Weitz *et al.*, 1985). At constant temperature, the Brownian velocity is inversely proportional to the square root of mass of nanoparticles and aggregates. The scale of size distribution governs diffusion of aggregates in the nanofluid and the sticking probability of particles and clusters. In the absence of convection, diffusion becomes the rate-limiting step leading to aggregate formation.

Nanoclusters

A model for the effective thermal conductivity of the nanofluid that accounts for agglomeration of spherical nanoparticles was developed by combining the effective medium approximation (Maxwell model) and the Fractal theory for description of nanoparticle aggregates or clusters (Wang *et al.*, 2003). The Fractal theory was developed based on the scale invariant nature of the aggregates or clusters. Equation 2 describes this Fractal model and takes into account the thermal conductivity of nanoparticle clusters (k_{cl}) and the number distribution of those clusters (n) as a function of cluster radius (r_{cl}). The effective thermal conductivity of the nanofluid in the Fractal model is determined by integrating the thermal conductivity of clusters and number of clusters.

$$\frac{k_{eff}}{k_f} = \frac{(1 - \varphi) + 3\varphi \int_0^\infty \frac{k_{cl}(r_{cl}) \cdot n(r_{cl})}{k_{cl}(r_{cl}) + 2k_f} dr_{cl}}{(1 - \varphi) + 3\varphi \int_0^\infty \frac{k_f \cdot n(r_{cl})}{k_{cl}(r_{cl}) + 2k_f} dr_{cl}} \rightarrow (2)$$

The size of the nanoparticle aggregates or clusters are not exactly spherical, and r_{cl} refers to the radius of gyration of the aggregate. Equation 3 defines the number of clusters based on log normal particle size distributions determined by dynamic light scattering, with the value of σ set to 1.5 and r_p representing the particle radius (Thomas, 1987).

$$n(r_{cl}) = \frac{1}{r_{cl}\sqrt{2\pi} \cdot \ln(\sigma)} \cdot \exp \left\{ - \left[\frac{\ln(r_{cl}/r_p)}{\sqrt{2\pi} \cdot \ln(\sigma)} \right]^2 \right\} \rightarrow (3)$$

The thermal conductivity of nanoclusters can be predicted as a function of cluster size using the Bruggeman model (Bruggeman, 1935 and Wang *et al.*, 2003). In equations 4 and 5, φ^* is the volume fraction of clusters of size r_{cl} , and is computed using the expression $\varphi^* = (r_{cl}/r_a)^{D-3}$, where D is the fractal dimension. For diffusion-limited cluster-cluster aggregation (DLCCA) mechanism of cluster formation, the fractal dimension (D) is determined to be 1.85 (Özerinç *et al.*, 2009).

$$k_{cl} = (3\varphi^* - 1)k_p + [3(1 - \varphi^*) - 1]k_f + \sqrt{\Delta} \rightarrow (4)$$

$$\Delta = (3\varphi^* - 1)^2 k_p^2 + [3(1 - \varphi^*) - 1]^2 k_f^2 + 2[2 + 9\varphi^*(1 - \varphi^*)]k_p k_f \rightarrow (5)$$

Based on the Fractal model, it can be concluded that the extent of agglomeration drives the size of nanoclusters. The volume fraction of nanoclusters in that size range has a direct bearing on the thermal conductivity of the nanofluid.

Nanolayer

In addition to nanoparticle agglomeration, the liquid molecules closer to the surface of nanoparticles form a nanolayer, which acts as a thermal bridge between a particle and the bulk liquid. Because of this, the thickness of the nanolayer could play an important role in thermal conductivity enhancement of the nanofluid. The Structural model of nanofluids is considered to consist of solid nanoparticle cluster, bulk liquid, and a nanolayer surrounding the particle (Yu and Choi, 2003). The thermal conductivity equation based on the Fractal model is modified to account for total nanolayer thickness, radius of the cluster, and thermal resistance

of the interfacial layer in the region between the particle and the bulk fluid (Xie *et al.*, 2005). Figure 1 shows a representative sketch of an aggregate of size, r_{cl} with thermal conductivity, k_{cl} , surrounded by an interfacial layer of thickness δ .

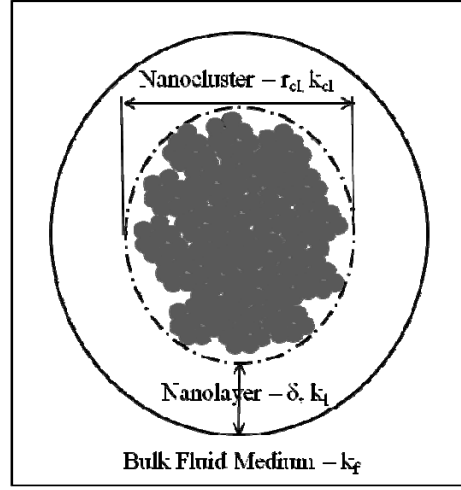


Fig 1 Structural Model of Nanoclusters, Nanolayer, and the Bulk Fluid Medium

The complexity of the physiochemical interactions are avoided by assuming that the thermal conductivity of the interfacial layer, $k(r)$, varies linearly from the surface of the nanoclusters to the bulk fluid, where $r_{cl} \leq r \leq r_{cl} + \delta$. The modified thermal conductivity distribution, $k(r)$, inside the nanolayer is shown by Equation 6 and the modified thermal resistance, R_{layer} , of the interfacial layer is shown by Equation 7. The thickness of the nanolayer in Equation 8 is dependent on the properties of the base fluid and is not affected by the new Structural model. The thermal conductivity of the interfacial layer, k_l , is shown by Equation 9. M_f is the molecular weight, and ρ_f is the density of the base fluid. N_A denotes the Avogadro's constant. Equations 6–9 were proposed by Xie *et al.* (2005).

$$k(r) = \left[\frac{k_f - k_{cl}}{\delta} \right] \cdot r_{cl} + \left[\frac{k_{cl} \cdot (r_{cl} + \delta) - k_f \cdot r_{cl}}{\delta} \right] \rightarrow (6)$$

$$R_{layer} = \int_{r_{cl}}^{r_{cl} + \delta} \frac{dr}{4\pi r^2 k(r)} \rightarrow (7)$$

$$\delta = \frac{1}{\sqrt{3}} \cdot \left[\frac{4M_f}{\rho_f N_A} \right]^{1/3} \rightarrow (8)$$

$$k_l(r_{cl}) = \frac{\delta}{r_{cl} \cdot (r_{cl} + \delta) \cdot [4\pi R_{layer}]} \rightarrow (9)$$

The thermal conductivity of the aggregate (Equations 4 and 5) can be modified to include the thermal conductivity of the interfacial layer. This modification is done by replacing k_p in Equations 4 and 5 with k_{cp} , as shown in Equation 10 (Özerinç *et al.*, 2009).

$$k_{cp} = k_l \frac{(k_p + 2k_l) + 2A^3(k_p - k_l)}{(k_p + 2k_l) - A^3(k_p - k_l)} \rightarrow (10)$$

$$A = 1 - \frac{\delta}{\delta + r_p} \rightarrow (11)$$

In Equations 2, 4, and 5, (r_p+t) , $[(r_p+t)/r_p]^3 \varphi$ and k_{cp} should be substituted for r_p , φ , and k_p , respectively, when both agglomeration and interfacial layer are used to account for effective thermal conductivity of the nanofluid.

Objective

This paper focuses on the effect of diffusion-limited cluster–cluster aggregation (DLCCA) mechanism on thermal conductivity of alumina nanofluids in de-ionized water, at 0.2 percent and 1 percent by volume, in the presence of nanolayer around the aggregates. This study reports the size distribution of aggregates at regular (1 percent) and dilute (0.2 percent) particle volume fractions measured using DLS experiments. The effective thermal conductivities were determined using the Maxwell, Fractal, and Nanolayer models at both regular and dilute concentrations and have been compared to determine the impact of clustering and nanolayer formation. The study concludes by examining whether the relationship between thermal conductivity and particle volume fraction is preserved across all the thermal conductivity models, and it determines whether nanocluster or nanolayer becomes the dominant mechanism that contributes to enhancement in thermal conductivity of the nanofluid.

Materials and Methods

Nanoparticles and Nanofluids

Alumina nanofluid is prepared using a two-step method. In the first step, Nanophase Technologies Corporation[®] manufactured alumina nanoparticles with an average particle radius of 20 nm using a Physical Vapor Synthesis method.

This method is commonly used for producing large quantities of nanocrystalline materials due to its accurate and precise control over particle size, purity, and low cost (Ford, 1998). Colloidal suspensions of nanofluids were prepared by dispersing 1.4780 grams of the alumina nanoparticles into 20 mL of de-ionized water in a vial, and the contents of the vial were mixed in a shaker. Added to the vial were 1.4315 grams of benzethonium chloride (BZT), followed by dilution with de-ionized water until the concentration of alumina in the solution was 1.05 percent by volume. The solution was placed in a water bath and thoroughly mixed by an ultrasonic probe at 40 watts for 10 minutes using an Omni Sonic Ruptor 400 Ultrasonic Homogenizer, which was manufactured by Omni International[®]. An ultrasonic probe was chosen, based on its ease of use and performance, for agglomerating particles [Huang *et al.*, 2008; Nasiri *et al.*, 2011]. This solution was then used for dilutions with de-ionized water to obtain multiple samples at 0.2 percent by volume alumina concentrations. The dilutions were then resonicated at 40 watts for 30 minutes prior to aggregate size measurement using the DLS technique.

Nanofluids Characterization: DLS

The effect of nanoparticle agglomeration and nanolayer structure on thermal conductivity of the nanofluid can be investigated using the DLS technique to provide data on volume fraction of clusters as a function of cluster radius. DLS measurements are performed using the Zetasizer Nano Series[®] instrument and 0.5 ml of the representative nanofluid sample. The instrument performs size measurements based on the Brownian motion of aggregates, and relates it to the size of the particles. The particles are illuminated with a monochromatic laser light. The intensity fluctuations in the scattered light are analyzed for volume and number distributions of nanoparticle clusters. The Zetasizer Nano System measures the rate of intensity fluctuations due to movement of aggregates and calculates the size of the aggregates. The fundamental size distribution generated is an intensity distribution and is converted using the Mie theory to a volume distribution. The Zetasizer instrument is programmed to provide an output containing volume distribution as a function of nanoparticle cluster radius. The Non-Invasive Back Scatter (NIBS) technique is used to obtain the volume fraction-size distributions. The process by which data was collected is shown in

Figure 2. The NIBS technique is defined by the angle at which the detector collects the scattered light. For the NIBS technique, the back scatter angle is 173° . The helium neon laser (1), with a wavelength of 632.8 nm, is passed through an attenuator (2) to reduce the beam intensity, prior to sample illumination (3). The detector (4) is positioned at 173° to collect the scattered light. The volume distribution, size data is obtained from the Zetasizer instrument software, after signal processing and correlation by the digital signal processor (correlator) (5).

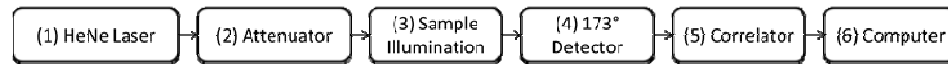


Fig 2 Non-Invasive Backscatter DLS Measurement

Results and Discussion

For purposes of this discussion, 1.05 percent and 0.21 percent by volume nanofluids will be referred to as regular and dilute nanofluids, respectively. Three sets of DLS measurements were conducted on regular and dilute nanofluids. The averaged volume distribution of the clusters as a function of aggregate radius obtained using DLS measurements is shown in Figure 3.

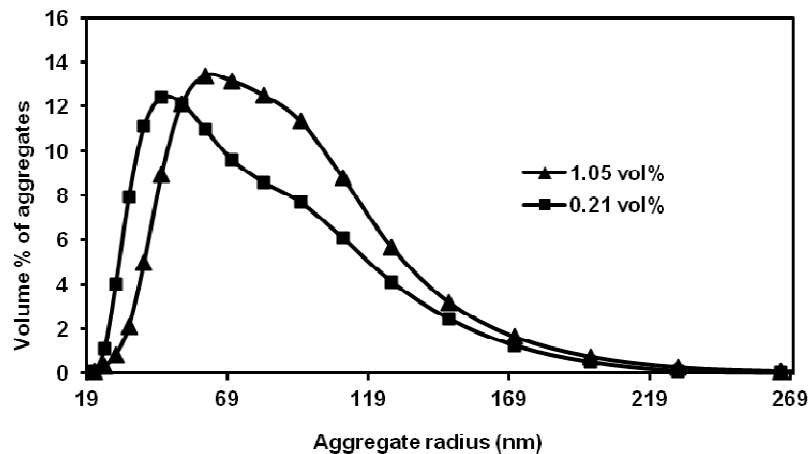


Fig 3 Aggregates Size Distribution in the Nanofluids

The aggregate volume fraction for dilute nanofluid peaks at 12.4 percent at a radius of 45.64 nm. Nanoparticles in solution collide due to Brownian motion to form aggregates with a radius greater than 20 nm. With the increasing size, the velocity of the aggregates is reduced, resulting in decreased diffusion. For dilute nanofluids, the low diffusion of aggregates combined with low particle

concentration results in lower collision probability and low volume fraction of aggregates above 45.64 nm. For regular nanofluids, the volume fraction peak occurs at 13.38 percent at 61.21 nm. It should also be noted that there is a higher volume fraction of aggregates in a regular nanofluid beyond 45.64 nm compared to dilute nanofluid. In regular nanofluids, while the aggregate diffusion is lower at higher radii, the number of particles is five times higher compared to dilute nanofluids, thereby increasing the probability of collision to form larger aggregates. Thus, the majority of the smaller aggregates that were formed in a regular nanofluid collides and sticks to form larger aggregates, causing the peak to shift from 45.64 nm to 61.21 nm. The significance of this result is that with the overall increase in volume fraction and number of particles, DLCCA mechanism drives to form larger clusters at higher volume fractions. In the next few sections, this data will be applied to the aforementioned thermal conductivity models to determine the impact of aggregation on thermal conductivity. In comparing Figure 3 and Figure 4, it can be concluded that the cumulative volume percentages of smaller aggregates are higher for a dilute nanofluid as opposed to a regular nanofluid and that the higher concentrations of alumina nanoparticles leads to formation of larger clusters.

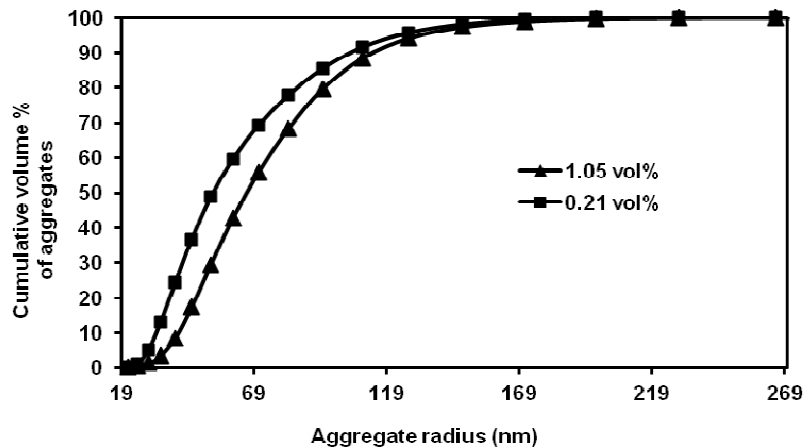


Fig 4 Cumulative Volume Fraction of Aggregates in the Nanofluid

The Maxwell model yields a thermal conductivity value of 0.6044 W/m.K and 0.6074 W/m.K for the regular and dilute nanofluids, respectively, with the respective percentage enhancements in thermal conductivities, from the base fluid, being 3 percent and 0.6 percent for the two nanofluids. The number of particles in a single aggregate can be evaluated using $N = (r_c/r_a)^D$, where $D = 1.85$ for

DLCCA process. Figure 5 shows that as the radius of the aggregate increases thirteen fold, from 20 nm to 260 nm, the number of particles per aggregate increases to a maximum of 120 with the Brownian velocity dropping below 50 m/s. This decrease in velocity decreases diffusion, and thereby limits larger aggregates from further growth.

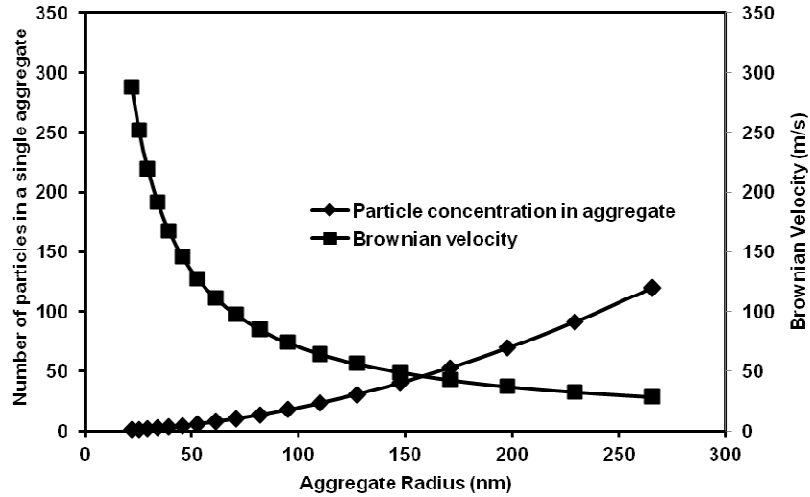


Fig 5 Particle Concentration per Aggregate and Brownian Velocity

Figure 6 shows the volume fraction of nanoparticles in a single aggregate (ϕ^*), as illustrated by Equations 4 and 5, and this is related to the number of particles per aggregate (N) by the relation, $\phi^* = N(r_d/r_{cl})^3$. While the maximum hydrodynamic radius of the aggregate is approximately 265 nm, the total number of particles at that size remains around 120 nm. This shows that with increase in hydrodynamic radius, the aggregate becomes less compact. Therefore, the hydrodynamic radius of the aggregate is a cluster of aggregated nanoparticles containing base fluid within the cluster, and the resulting percolating clusters (Prasher *et al.*, 2006) are analyzed for enhancement of the thermal conductivity of the nanofluid.

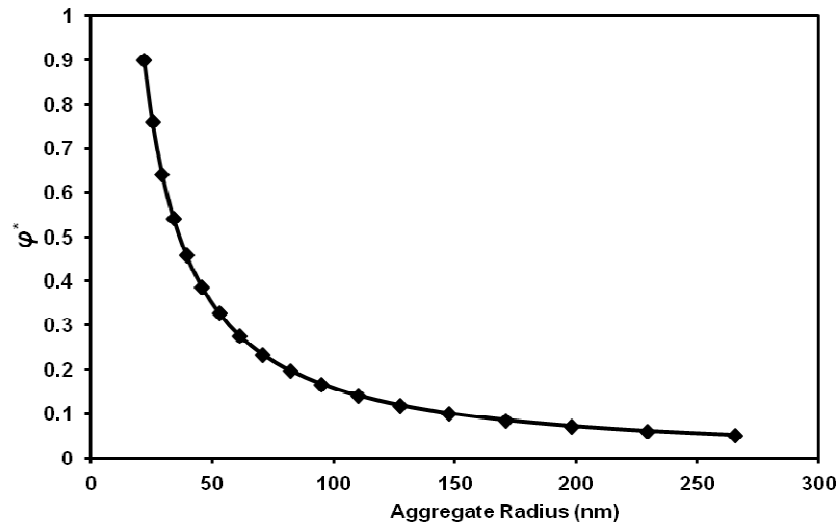


Fig 6 Volume Fraction of Nanoparticles in a Single Aggregate

Table 1 lists the thermal conductivities of alumina nanofluids with particle concentrations at 1.05 percent and 0.21 percent that were evaluated using the Maxwell model, Fractal model, and combined Fractal and Nanolayer model. Figure 7 shows the percentage of enhancement in thermal conductivity for each of the three models relative to the base fluid, and Table 2 lists the percentage of enhancement in thermal conductivity for all the models.

Table 1 Model-Based Thermal Conductivities of Alumina Nanofluids

Particle Volume %	Thermal Conductivity (W/m.K)			
	Base Fluid	Alumina Nanofluid		
		Maxwell Model	Fractal Model	Fractal and Nanolayer Model
1.05	0.5868	0.6044	0.6298	0.6312
0.21	0.6038	0.6074	0.6127	0.6130

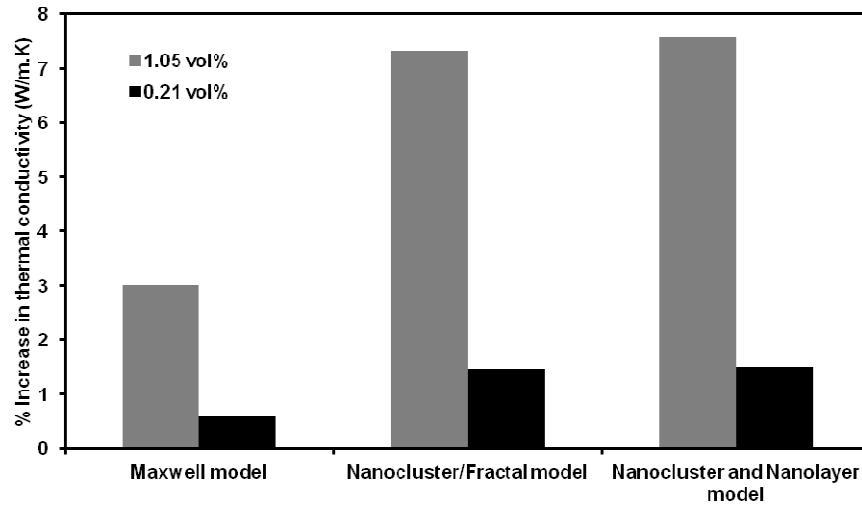


Fig 7 Thermal Conductivity Enhancements of Nanofluids

Table 2: Percentage of Enhancement in Thermal Conductivity of Alumina Nanofluids

Particle Volume %	Thermal Conductivity Enhancement (%)		
	Maxwell Model	Fractal Model	Fractal and Nanolayer Model
1.05	3.0020	7.3211	7.5698
0.21	0.5946	1.4649	1.5151

As we move from a nanofluid containing completely dispersed nanoparticles to a nanofluid with aggregation and percolating clusters, the thermal conductivity of the clustered regular nanofluid is 2.44 times greater than a completely dispersed nanofluid. When liquid layering around percolating clusters is considered, the thermal conductivity of the regular nanofluid increases to 2.52 times greater than that of a completely dispersed nanofluid. For dilute nanofluid, thermal conductivities were enhanced 2.47 times for fluid with percolating clusters and enhanced 2.55 times for percolating clusters with liquid layering around clusters. The results indicate that thermal conductivity increases by approximately the same amount for both dilute and regular nanofluids as we move from well-dispersed condition to percolating clusters and liquid layering around aggregates. The results also indicate that liquid layering around nanoparticle clusters does not additionally contribute to significant increases in thermal conductivity of the nanofluid. The ratio of enhancement in thermal conductivity between well-dispersed nanofluid and aggregated system with or without liquid layering is the

same regardless of nanoparticle concentration, over-dilute and regular concentration regimes.

For well-dispersed nanofluid, the thermal conductivity increases by approximately five times as the nanoparticle volume concentration increases from 0.21 percent in a dilute nanofluid to 1.05 percent in a regular nanofluid. The results show that thermal conductivity increases five fold for both the percolating cluster model and the cluster-liquid layering model as the particle concentration increases five fold from regular to dilute nanofluid. This indicates that the linear relationship between thermal conductivity enhancement and particle concentration is well-preserved for nanofluids that are well-dispersed and for nanofluids that have percolating clusters with and without liquid layering. Thus, sensitivity to concentration is the same across different mechanisms of particle interaction in the nanofluid.

Conclusions

The research study focused on dilute and regular nanofluids with 0.21 percent and 1.05 percent by volume concentration of alumina nanoparticles. The nanofluids were characterized using DLS measurements to obtain percentage volume distribution as a function of hydrodynamic aggregate radius. It was concluded that the lack of a sufficient number of nanoparticles at dilute concentration reduced the collision probability and growth of larger percolating clusters. The DLS results were used to compute the effective thermal conductivity of nanofluids using percolating clusters and liquid layers around aggregates, and compare it to a well-dispersed alumina nanofluid. It was concluded that the thermal conductivities of both dilute and regular nanofluids increased approximately 2.5 fold compared to a well-dispersed nanofluid, and that the contribution of liquid layering to enhancement in thermal conductivity is negligible for all practical purposes. It was also concluded that a near-linear relationship between concentration and thermal conductivity is preserved for nanofluids that were well-dispersed, and with percolating clusters and liquid layering. Thus, agglomeration with percolating clusters accounted for a significant increase in thermal conductivity of nanofluids across dilute and regular concentration regimes. Based on the results, agglomeration of nanoparticles was determined to be a dominant factor in the overall thermal conductivity enhancement of nanofluids. By manipulating the size of the percolating clusters and volume distribution, nanofluids can be engineered

for applications that require specific thermal conductivities for use in ground vehicles.

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